High Temperature Engine Materials: Valve Materials Subtask

G. Muralidharan

Email: muralidhargn@ornl.gov

Phone: 865-574-4281

Oak Ridge National Laboratory
National Transportation Research Center

2018 U.S. DOE Vehicle Technologies Office
Annual Merit Review

June 20, 2018 Project ID: MAT053

This presentation does not contain any proprietary, confidential, or otherwise restricted information

ORNL is managed by UT-Battelle
for the US Department of Energy

OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Subtask Overview
New alumina-forming alloys for exhaust valves

Timeline

- Project start: October 2015
- Project end: September 2019
- Percent complete: 70%

Budget

- Total project funding Received
  - DOE 100%
- FY17 Funding: $ 215K
- Funding anticipated
  FY18: $ 240 K

Barriers

Barriers Addressed

- Changing internal combustion engine regimes
  - **Higher power density engines leading to higher peak exhaust valve temperatures**
- Long lead-times for materials commercialization
- Cost of the high performance alloys

Targets

- Improve passenger vehicle fuel economy by 25%
- Improve commercial vehicle engine efficiency at least 20%

Industry Advisors/Collaborators

- Lead: ORNL
- Carpenter Technologies- Materials Supplier
- Haynes International-Materials Supplier
- Argonne National Laboratory

Relevance and Objectives

- Exhaust gas temperatures are on the rise and are expected to continue to increase in future higher efficiency advanced engines
  - Temperatures are expected to increase from 870^{o}C to 950^{o}C by 2025 and to 1000^{o}C by 2050* in light-duty vehicles

- There is a critical need to develop materials that meet projected operational performance parameters but also meet *cost constraints*
- Objectives: Develop cost-effective exhaust valve alloys suitable for operating at temperatures up to 950^{o}C for use in advanced future engine concepts
  - Need good high temperature strength for valves: f(cylinder pressure, valve diameter, temp)
  - Oxidation resistance is critical

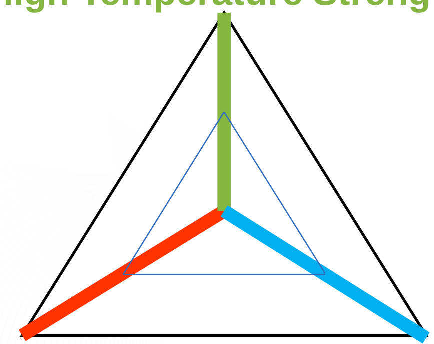
***DOE Vehicle Technologies Workshop report: Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion materials, Feb. 2013.**

FY17-FY18 Milestones

Month/ Year	Milestone Description	Status
Sep. 2017	**Down-select two alloys with the potential for at least 10% improvement in strength at 950 °C operation compared to commercial alloy Haynes®224 and good oxidation resistance**	**Completed**
Sep. 2018	**Identify one new low cost alumina-forming alloy** Identify one alumina-forming alloy and associated heat-treatment conditions to achieve at least a **2X improvement** and a **15% decrease in materials cost** over existing commercial alumina-forming alloys	**On-track**

Approach

- Current state-of-the-art commercial valve alloy 751, a chromia-forming alloy is
  - Primarily strengthened by coherent, intermetallic precipitates- γ' ($Ni_3(Al,Ti,Nb)$)
  - Does not have significant strength above ~850^{o}C due to dissolution of strengthening phase
  - Chromia-containing oxide forms *in-situ* and provides oxidation resistance
- A previous project developed lower cost chromia-forming alloys for use at 870 °C
- Current project aims to extend work to develop lower cost alloys for use at up to 950 °C
  - Strength decreases significantly at 950 °C
  - Oxidation behavior limits alloy design and performance
  - Alloy properties must be achieved at lowest cost



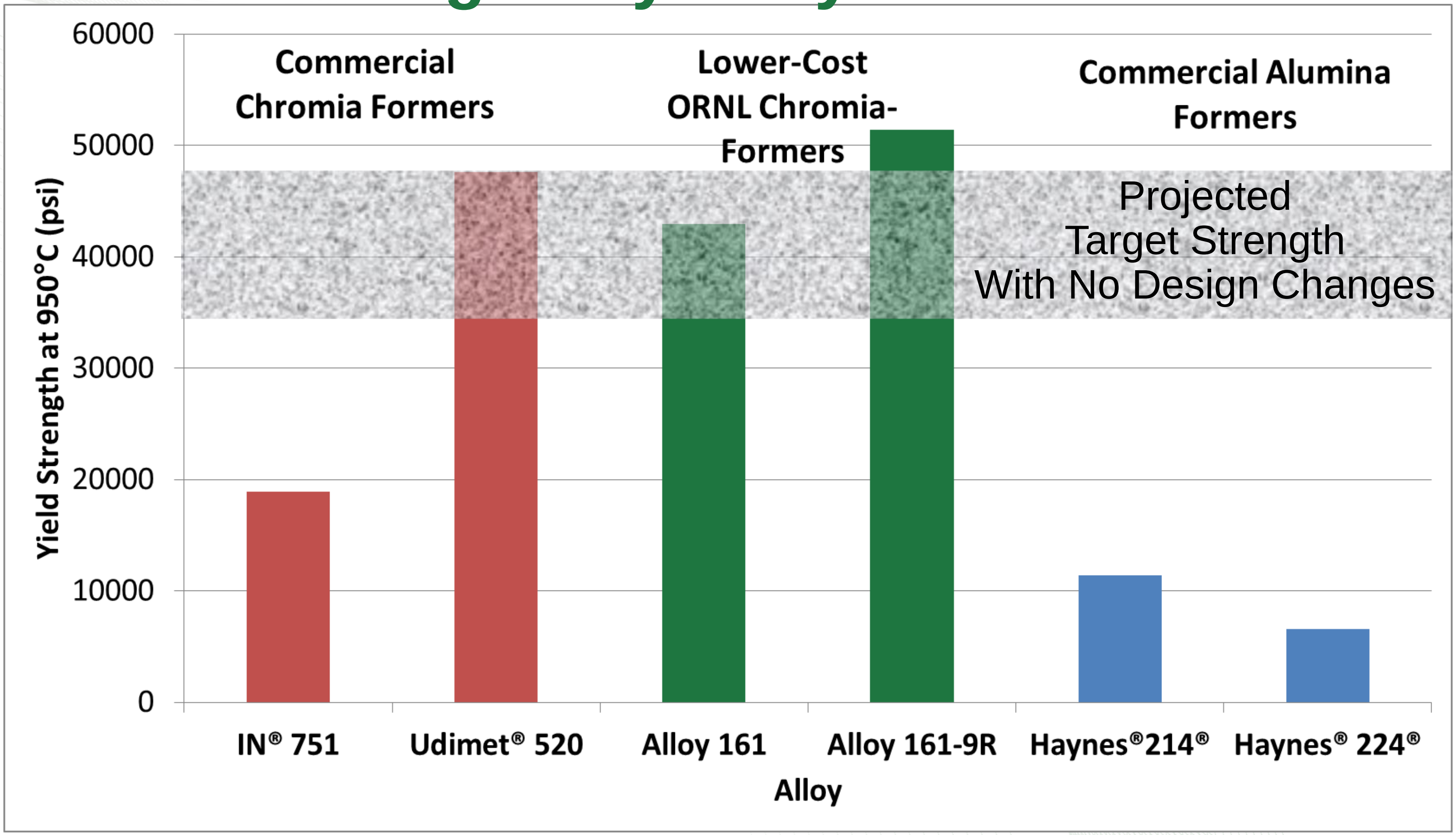
- Overall approach to alloy development:
  - Achieve a stable alumina (Al_2O_3) scale for superior oxidation resistance vs chromia-scale
  - Improve strength by increasing volume fraction and modifying other desirable characteristics (coherency etc.) of strengthening phases at 950 °C

Commercial Alloys of Interest are Ni-Based

Alloy	Ni	Co	Fe	Cr	Mo	Si	Mn	Al	Ti	W	C	Comments
IN ® 751	71.32	0.04	8.03	15.7	-	0.09	0.08	1.2	2.56	-	0.03	Chromia-former
Udimet® 520	57.65	11.7	0.59	18.6	6.35	0.05	0.01	2.0	3.0	-	0.04	Chromia-former
Haynes®214®	72.3	<0.15	3	16	<0.2	0.07	<0.5	4.5	<0.5	<0.5	0.04	Alumina-former
Haynes®224®	44.75	<2	27.5	20	<0.5	0.3	<0.5	3.6	0.3	<0.5	0.05	Alumina-former

- Chromia-formers primarily contain Cr + low Al
  - Insufficient oxidation resistance >850°C, high strength
- Alumina-formers contain lower Cr + high Al (> 3.0 wt. %)
  - Better oxidation resistance, lower strength
- Technical goal
  - Stronger, lower cost, alumina-forming alloys

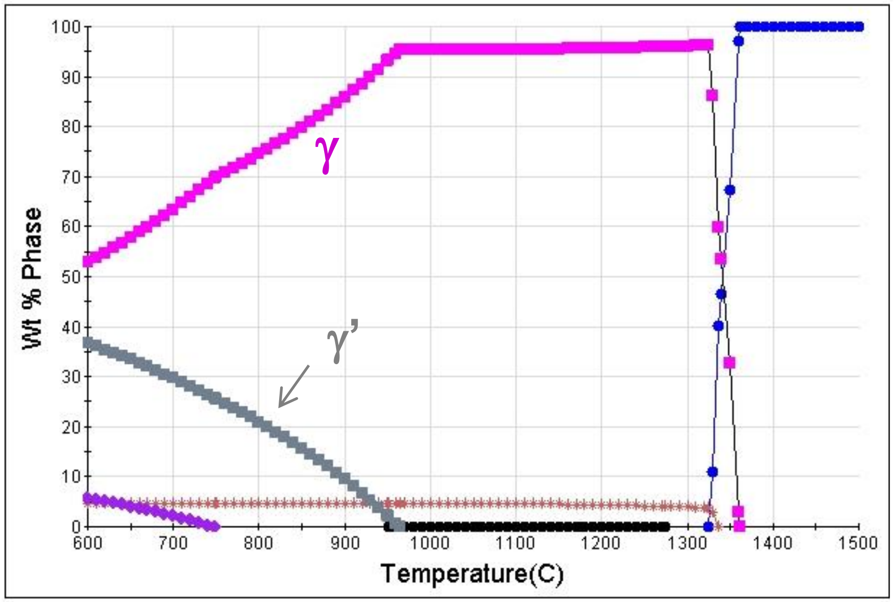
Use of Commercial Alumina-Forming Alloys is Limited by their Lower Strength Compared to Chromia-Forming Alloys Beyond 870°C



Chromia forming alloys exhibit poor oxidation resistance at ≥870^{o}C, thus existing alloys do not have the necessary combination of strength and oxidation resistance for valves at 950°C

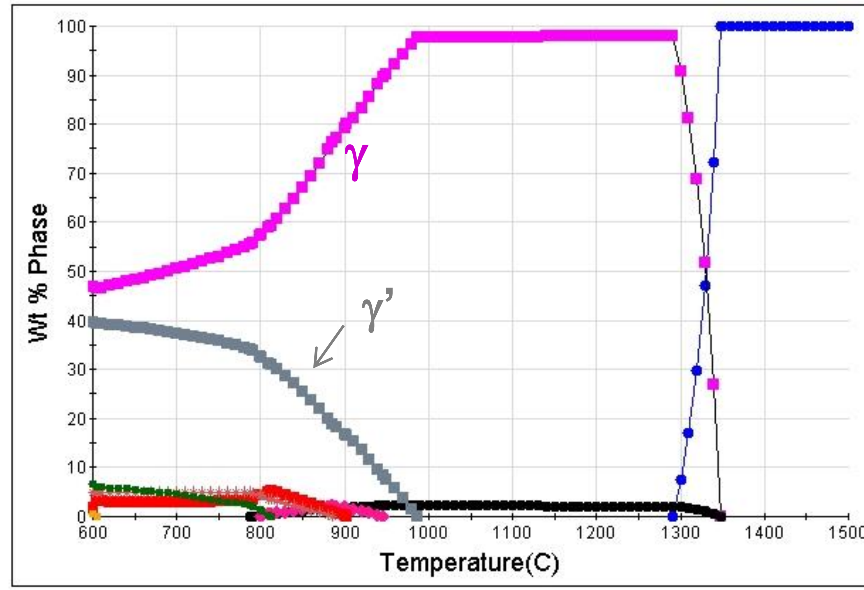
OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Achievements: Second Generation of ORNL Alumina-Forming Alloys Designed with Higher γ' contents and Lower Ni Levels



ORNL Alloy B

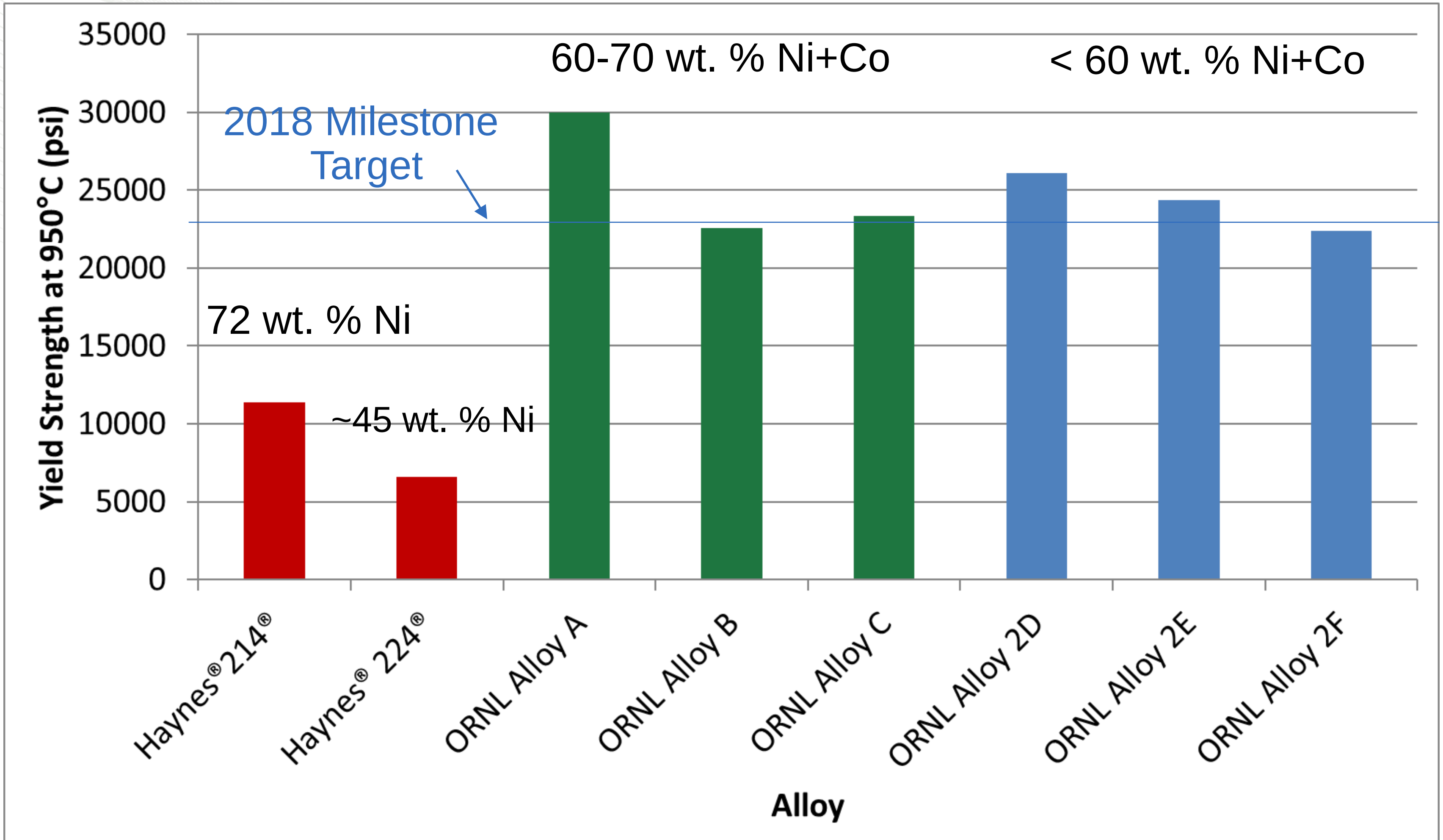
Wt. % γ' at 950°C: **~ 2.5 wt. %**
Ni: 60-70 wt. %



ORNL Alloy 2D

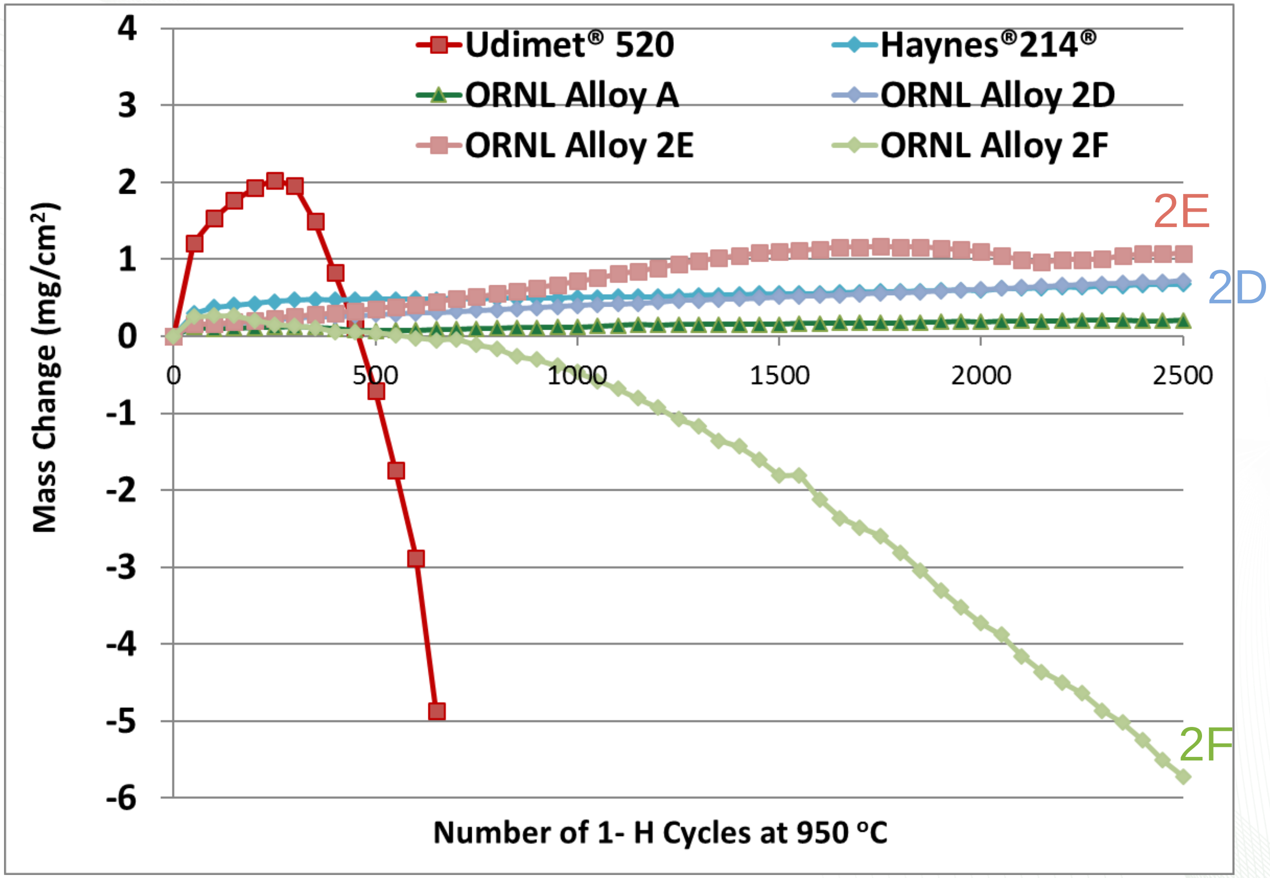
Wt. % γ' at 950°C: **~ 7.5 wt. %**
Ni: <60 wt. %

Accomplishments: Second Generation of ORNL Alumina-Forming Alloys Meet Milestone Target Strengths at 950°C at Even Lower Ni Content/Cost



Alloy strength at 950ºC needs further improvement to meet projected target of at least 35 ksi

Oxidation Resistances of Second Generation ORNL Alumina-forming Alloys at 950°C, Air+ 10% Water Vapor Vary With Composition



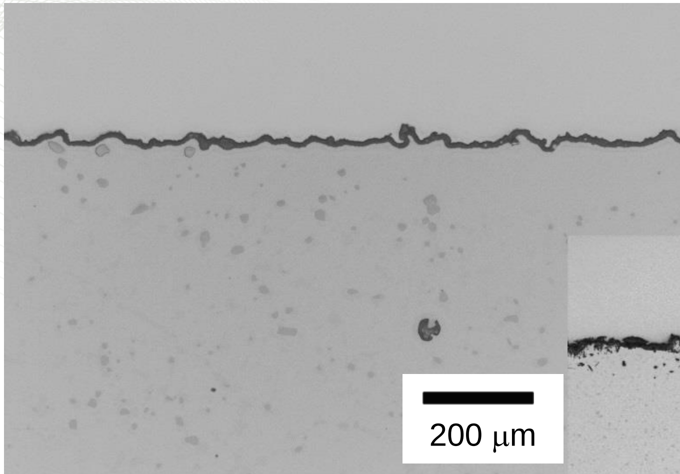
Low Mass Gain (Good)

Mass Loss (Bad)

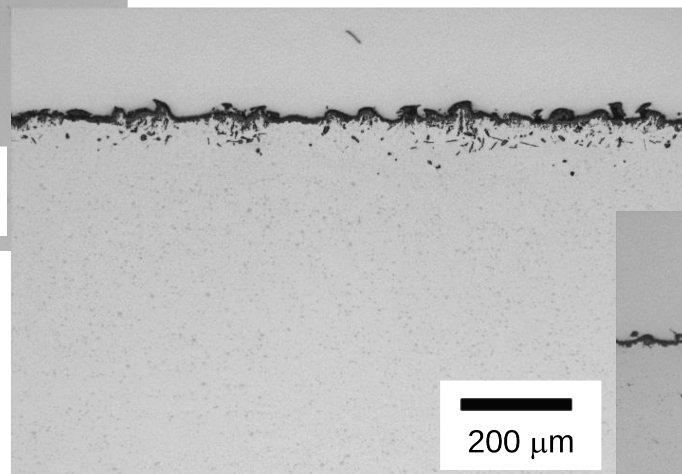
ORNL Alloy 2D Has >2X strength, good oxidation resistance at 950°C, and is lower in Ni levels compared to commercial alumina-formers

Cross-Sections of Alloys Show Differences In Oxide Formation

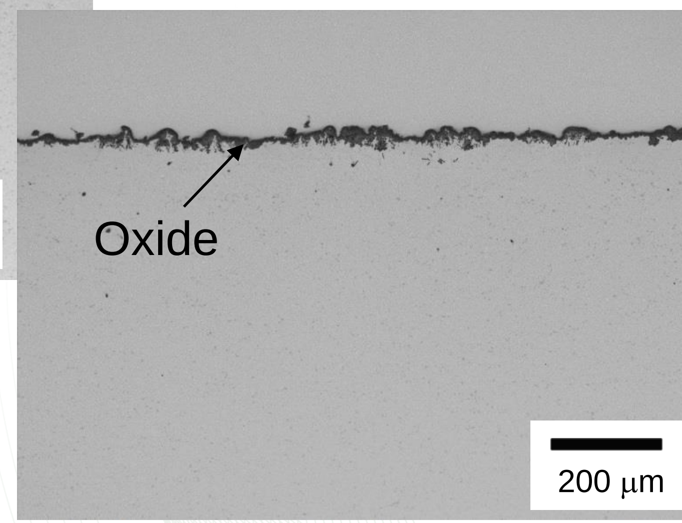
950°C, Air+ 10% Water Vapor, 2500 cycles



ORNL Alloy 2D
Thin Oxide Scale
No Internal Oxidation



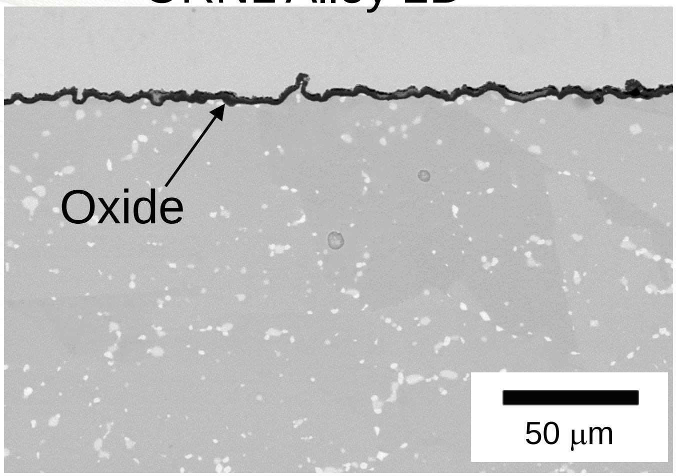
ORNL Alloy 2E
Thicker Scale
Internal Oxidation



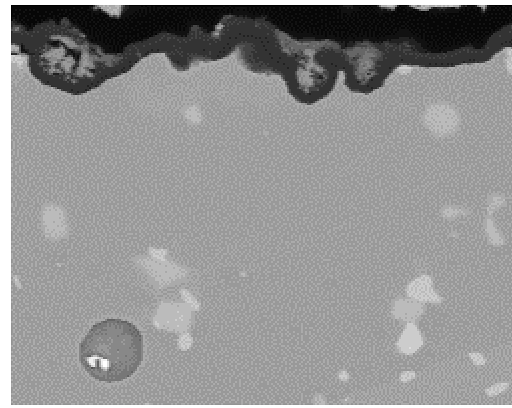
ORNL Alloy 2F
Thicker Scale

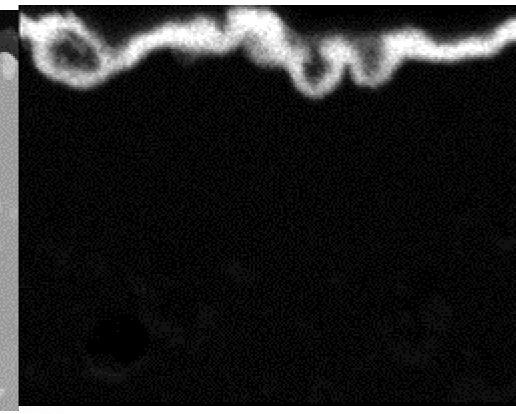
SEM/EDX Shows ORNL Alloy 2D Forms Continuous Aluminum Oxide Scale

ORNL Alloy 2D



950°C, Air+ 10% Water Vapor, 2500 hours

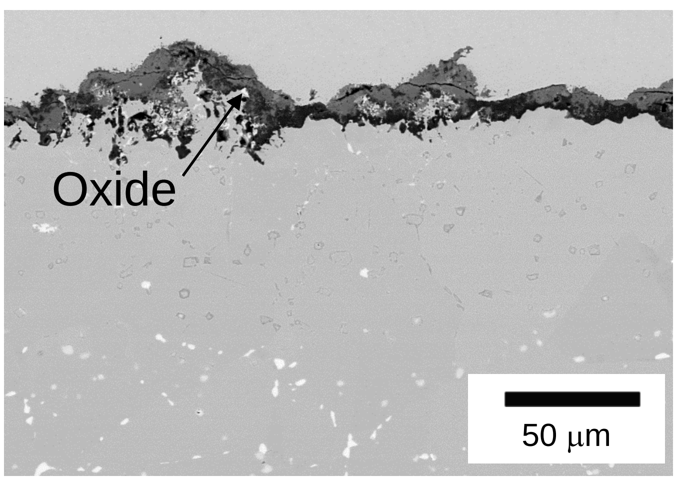


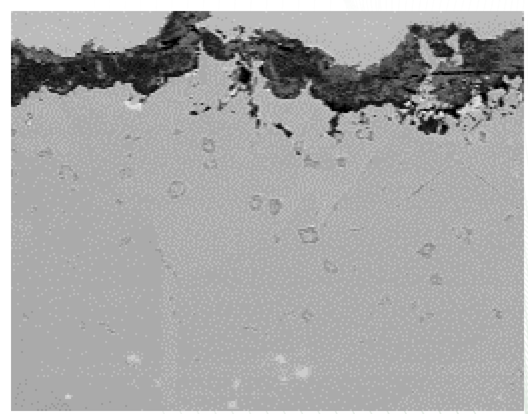


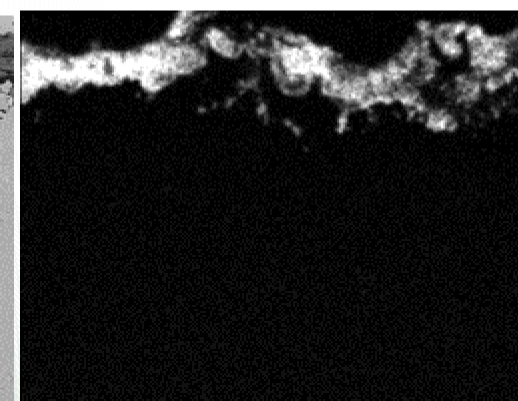
ORNL Alloy 2F

SE Image

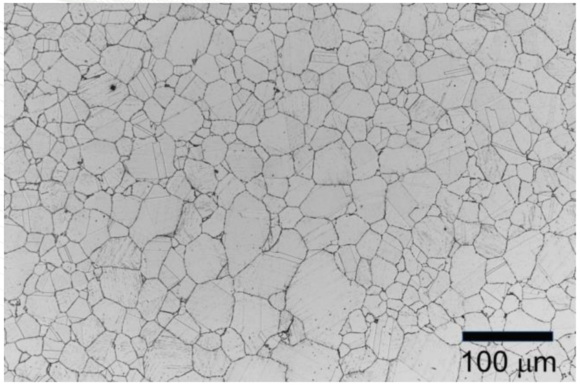
Al Map



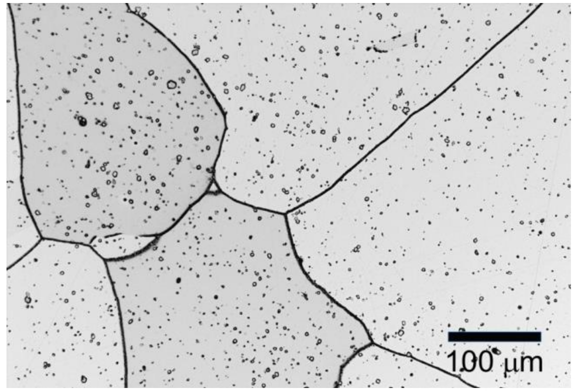




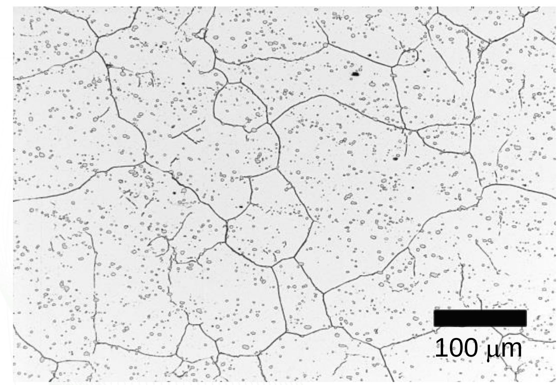
Second Generation ORNL Alumina-Forming Alloys Have Finer Grain Size Due to Better Microstructural Control



Haynes®214®
Average Grain Size ~18µm



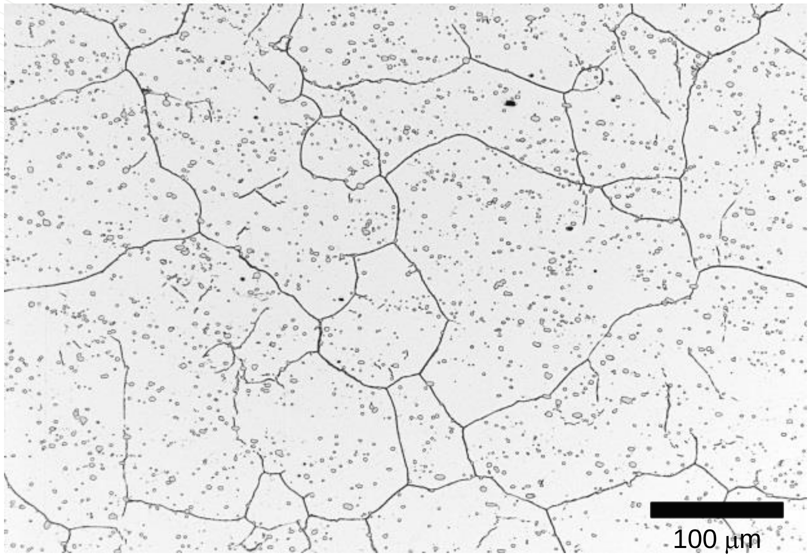
FY17
ORNL Alloy C
Average Grain Size ~640µm



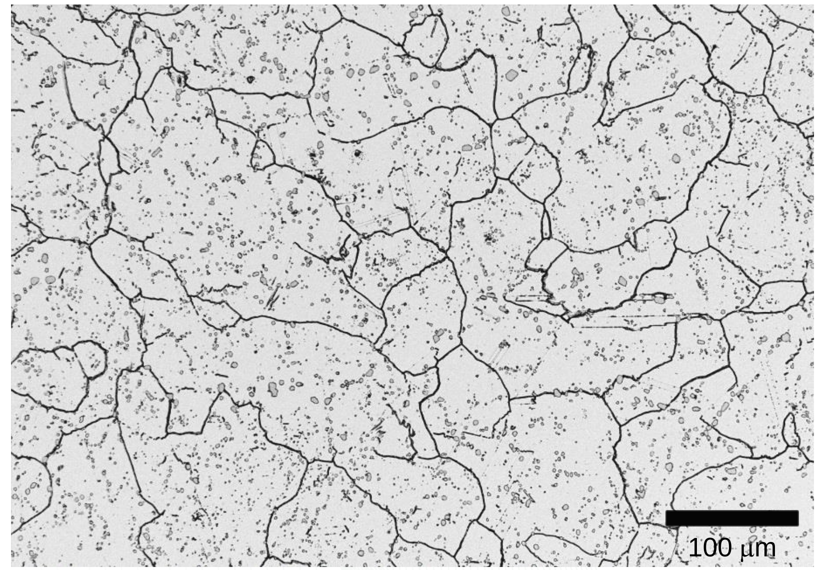
FY18
ORNL Alloy 2D
Average Grain Size~92µm

Better grain size control has been achieved in second generation ORNL alloys but further improvements possible

Accomplishments: New Heat-treatment Results In Finer Grain sizes



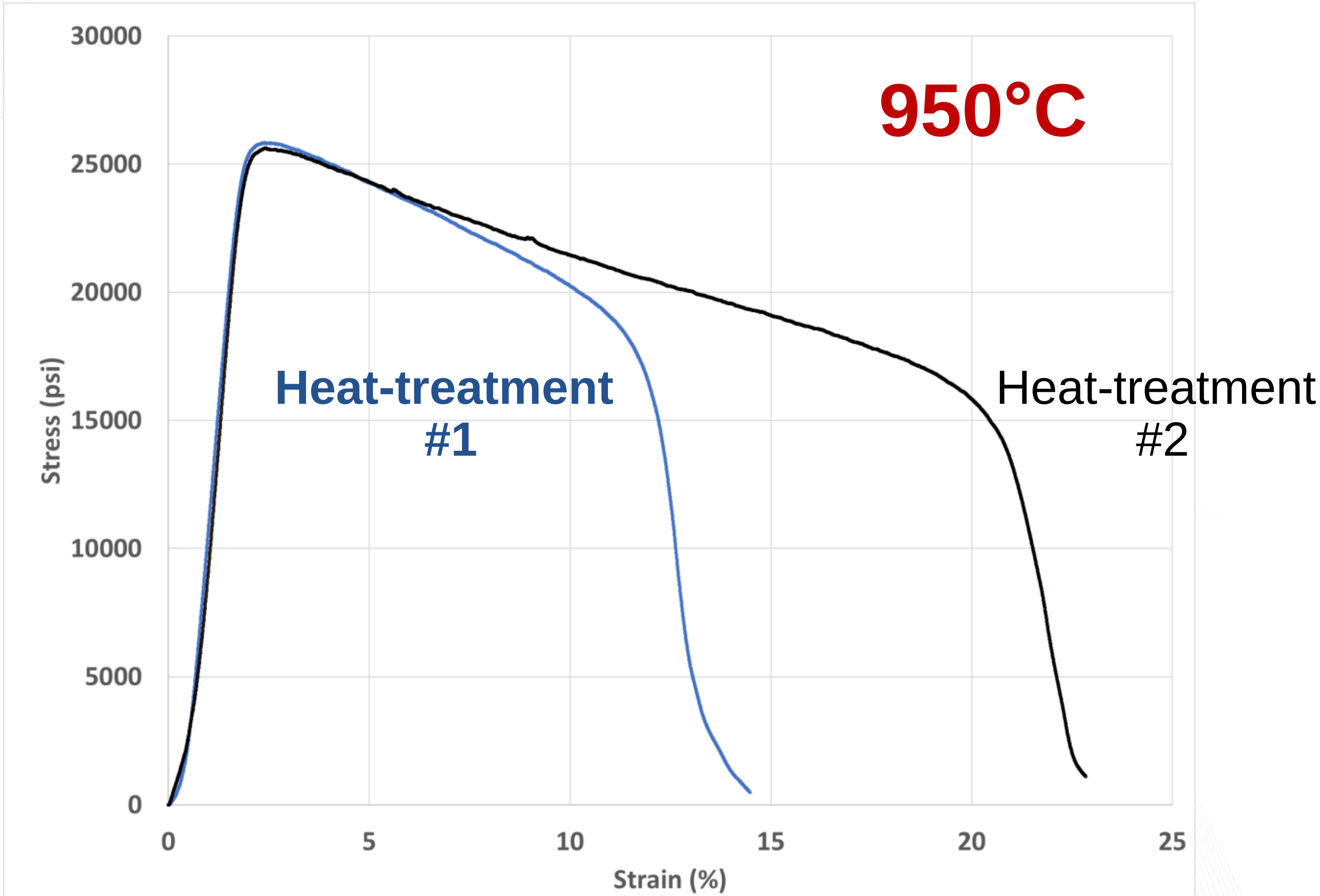
ORNL Alloy 2D
Prior Heat-Treatment
Average Grain Size ~92µm



ORNL Alloy 2D
New Heat-Treatment
Average Grain size ~ 60µm

Optimum grain size is required to balance high temperature strength, ductility, and creep properties

Ductility in ORNL Alloy 2D Improved with Modified Heat-Treatment



- **Yield strength not affected significantly by new heat-treatment**
- **Alloy has good ductility at all temperatures and can be forged into required shapes**

Response to Reviewer's Comments

Comment: The reviewer identified one concern in the approach, which was that the project is focused overall upon providing increased performance materials while remaining cost-effective; however, there did not appear to be any specific cost targets identified for the project. The reviewer noted that several proposed alloys appear to have comparable or slightly better costs than the baseline. The reviewer stated that the project should identify if comparable cost is the target, or if there is a price premium that might be considered acceptable to ultimate users

Response: Cost targets have been defined to be 15% lower than the baseline alloys. However, discussions with Tier 1 suppliers show that a price premium may be considered acceptable based upon the oxidation resistance requirements.

Comment: The reviewer agreed that newer engine combustion concepts mandate operation at higher in-cylinder pressures, but stated that the requirement of operational capabilities of the valves at higher temperatures was new information

Response: This information was obtained from the DOE Vehicle Technologies Workshop report: Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion materials, Feb. 2013 and through discussions with OEMs.

Comment: The reviewer stated that the mechanical property improvements appeared to be obtainable via microstructure improvement techniques, like heat treatment

Response: Significant strength improvements desired at these high temperatures in this class of alloys can only be achieved through increasing the role of stable precipitates at the operating temperature. While heat-treatment can affect initial microstructure, microstructural evolution has a significant effect on properties. Effect of grain size modifications through heat-treatment was demonstrated.

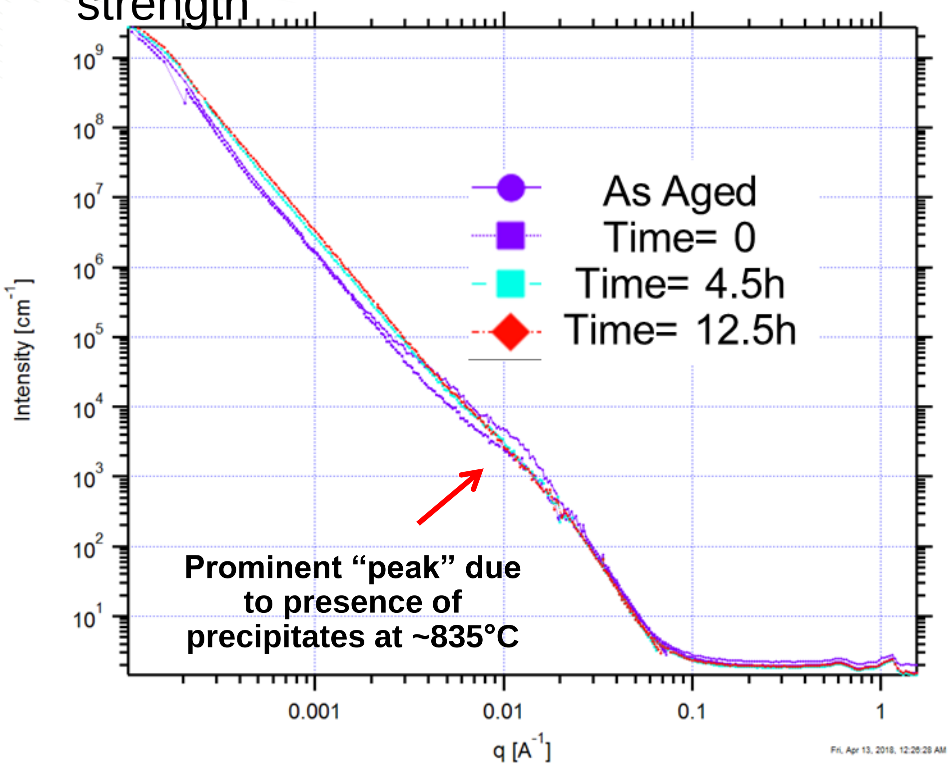
Collaborations and Coordination with Other Institutions

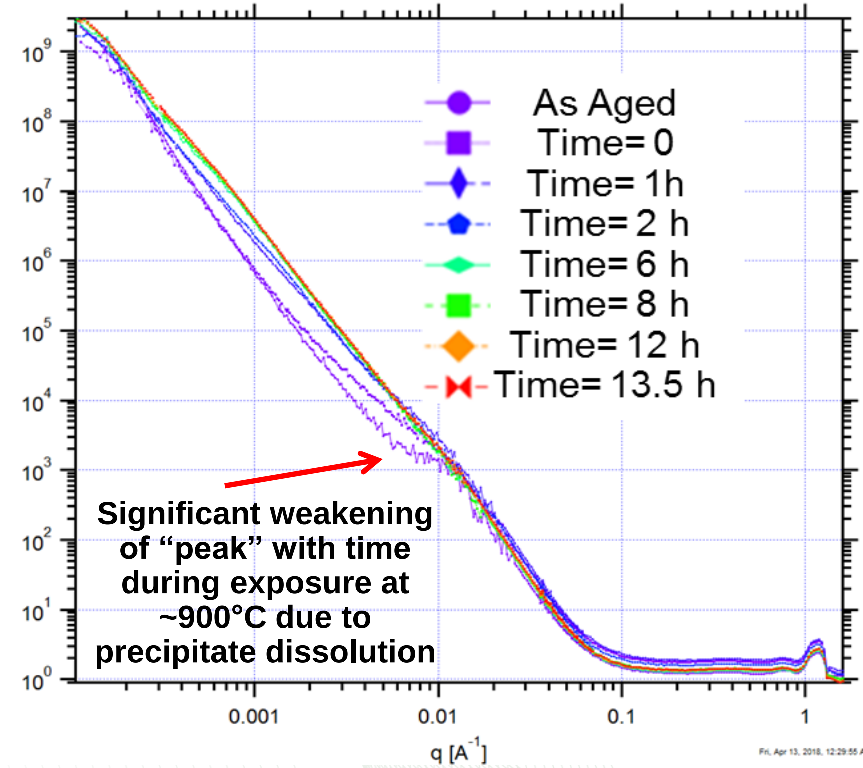
- **U. S. Patent 9,752, 468 B2***, G. Muralidharan*, "Low-Cost, High-Strength Fe-Ni-Cr Alloys for High Temperature Exhaust Valve Applications, Issued to ORNL, Sep. 5, 2017 from prior project on chromia-forming alloys for 870°C
- Collaborations with **Carpenter Technologies**
  - Potential for commercialization of patented alloys under discussion
- Collaborations with **Haynes Technologies**
  - Feedback received on best heat-treatment conditions and measured properties
  - Potential for fabrication of industrial scale heat, commercialization of patented and new alloys under discussion
- Collaborations with **Argonne National Laboratory** are on-going
  - Extended range Ultra Small-angle, Small-angle, and Wide-angle X-ray scattering facility to understand role of precipitation on strengthening
  - Powder diffraction facility for structure characterization

In-situ USAXS/SAXS showing particle size Evolution in ORNL 2E at Multiple Temperatures*

- *In-situ* Extended range Ultra Small-angle Scattering, and Small-angle scattering (USAXS/SAXS) is used to characterize γ' precipitate size after heat-treatment and its evolution during use

- Differences between alloys help understand effect of microstructural evolution on strength





*Collaboration with Matt Frith, Jan Ilavksy, and Saul Lapidus Argonne National Laboratory

Remaining Challenges and Barriers

- **Chromia-formers have the strength but do not have the oxidation resistance**
- **Further improvement in yield strength at 950°C for alumina-formers must be achieved to meet valve targets**
- Increase in yield strength must be achieved without loss of oxidation resistance
  - Ni levels must be kept low to achieve low costs
- Long term alloy stability must be evaluated
- Future alloys will have
  - Increased Al levels
  - Increased other strengthening elements
- Alloys must be evaluated for industrial scale processing
- Good strength and oxidation resistance must be achieved in alloys processed in industrial heats

Proposed Future Research

FY18/ FY19

- Further increased additions of alloy elements will be attempted to improve high temperature strength
- Oxidation resistance will be evaluated
- Most promising alloy will be down-selected
- Trial heats will be produced in industrial scale in collaboration with industrial adviser/industrial partner
- Testing of industrial scale heats will be performed

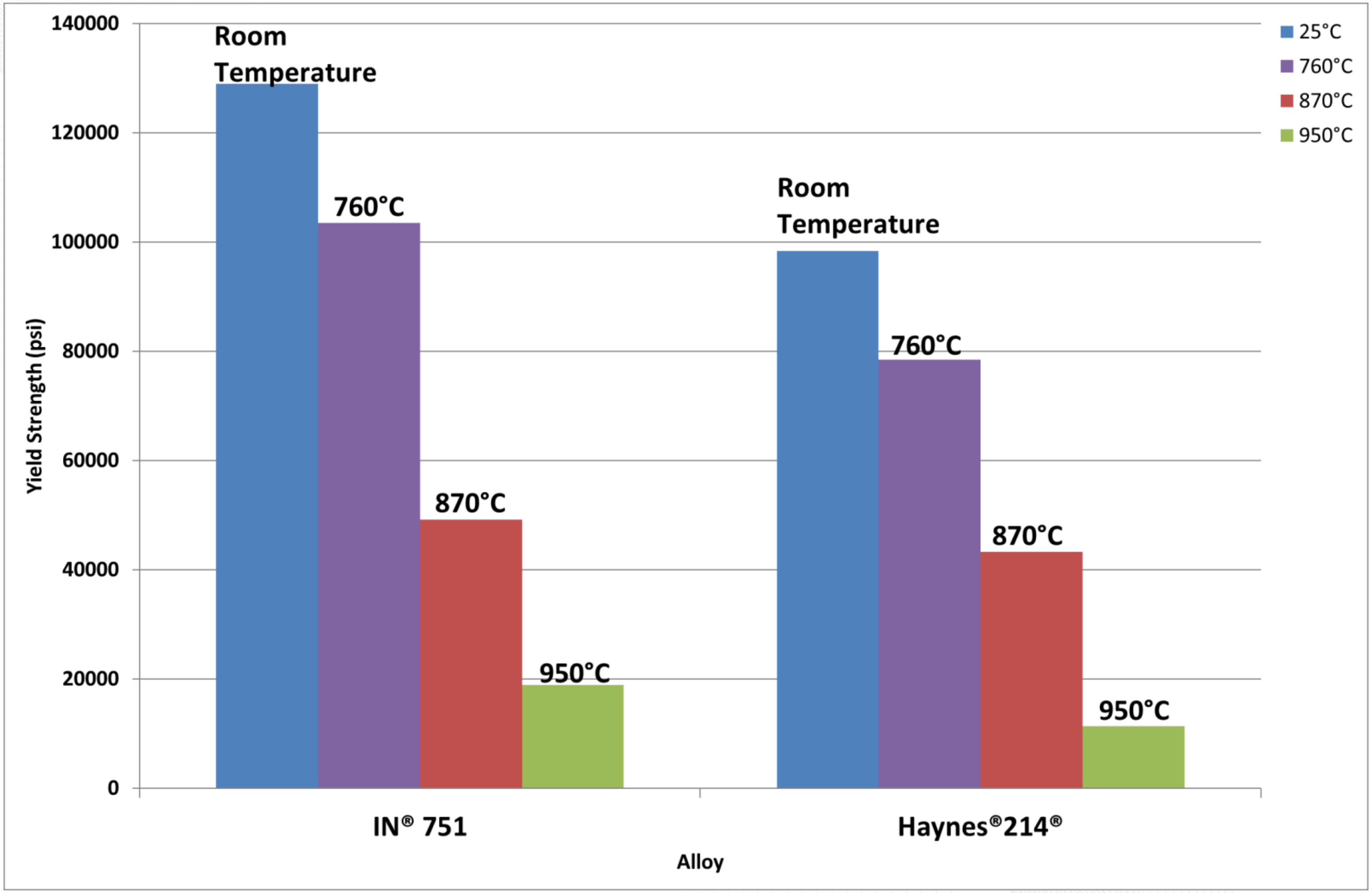
Any proposed future work is subject to change based on funding levels

Summary

- **Relevance:**
  - Temperatures are expected to increase from 870ºC to 950ºC in 2025 and to 1000ºC by 2050 in light-duty engines. Current valve alloy cannot meet strength and oxidation requirements for use at the higher temperatures and new cost-effect materials are needed for use at these temperatures.
- **Approach/Strategy**:
  - A computationally guided approach is being used to develop new higher strength alumina-forming alloys for use at 950ºC. A similar approach has been used previously to develop new cost-effective chormia-forming alloys for use at temperatures up to 950ºC.
- **Accomplishments:**
  - New alumina-forming alloys with oxidation resistance comparable to commercial alumina-forming alloys but with 2X yield strength at 950ºC and lower Ni-levels have been developed.
- **Collaborations:**
  - Collaborations are on-going with Carpenter Technologies, Haynes International, and Argonne National Laboratory
- **Proposed Future Work:**
  - One alloy will be down-selected for larger scale heats and further property evaluation. Paths for additional increase in yield strengths will be evaluated and new compositions will be developed.

Technical Back-up Slides

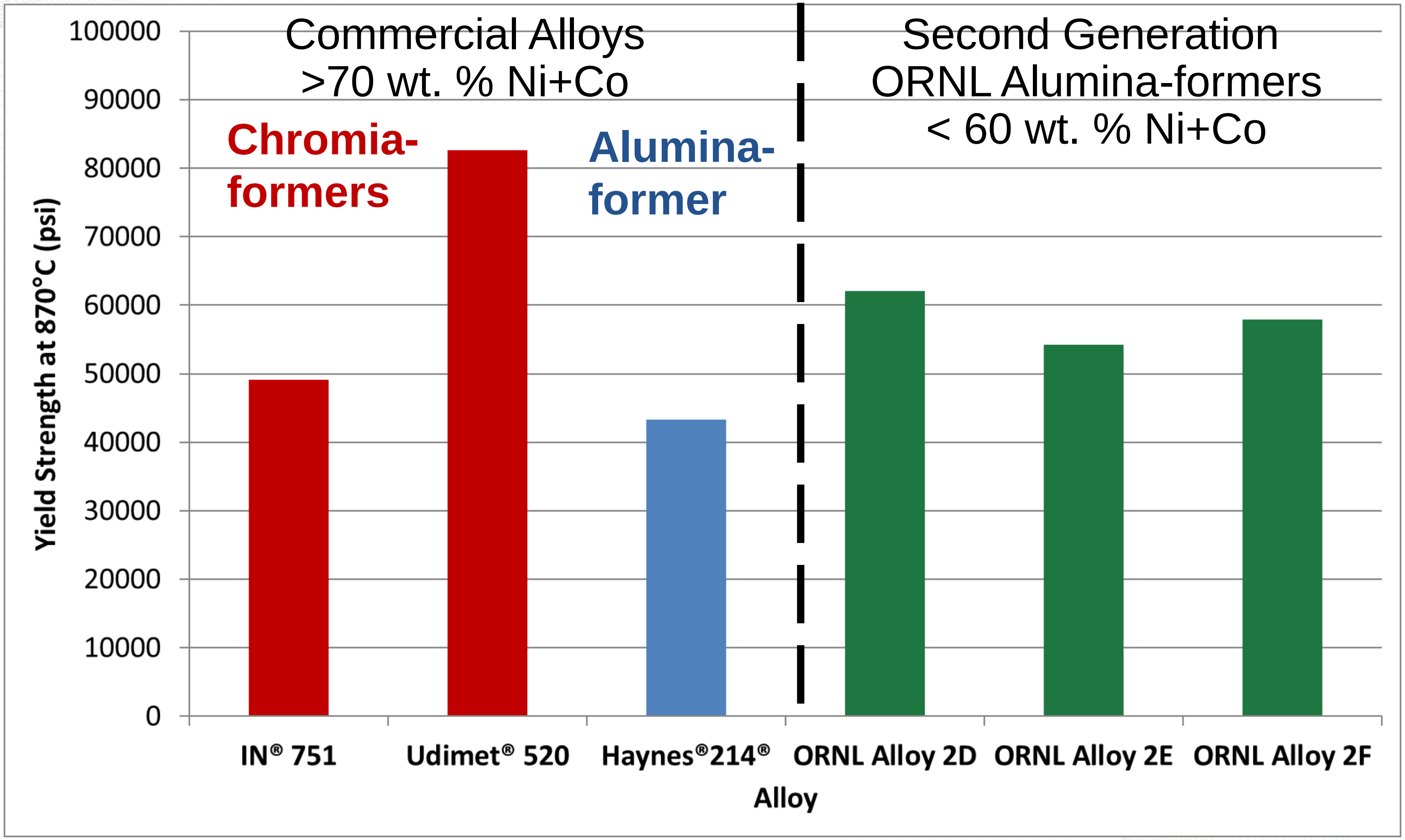
Temperature Dependence of Strength Varies With Alloy Composition



Chromia-forming IN®751 has higher strengths than Haynes ® 214 ® BUT it does not meet target strength properties at 950°C AND it has poor oxidation resistance at ≥870°C

OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

New ORNL Alloys Provide Lower Cost, Oxidation-Resistant Alternative to Alloy 751 at 870°C



New alumina-forming ORNL alloys have good strength at 870°C, better oxidation resistance than chromia-formers, and lower in cost